This Page Is Inserted by IFW Operations and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date 7 December 2000 (07.12.2000)

PCT

(10) International Publication Number WO 00/73231 A1

(51) International Patent Classification7:

C03C 13/00

(21) International Application Number: PCT/US00/14155

(22) International Filing Date:

23 May 2000 (23.05.2000)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data: 60/136,538

28 May 1999 (28.05.1999)

- (71) Applicant (for all designated States except US): PPG INDUSTRIES OHIO, INC. [US/US]; 3800 West 143rd Street, Cleveland, OH 44111 (US).
- (72) Inventor: and
- (75) Inventor/Applicant (for US only): WALLENBERGER,

Frederick, T. [US/US]; 9814 Three Degree Road, Allison Park, PA 15101 (US).

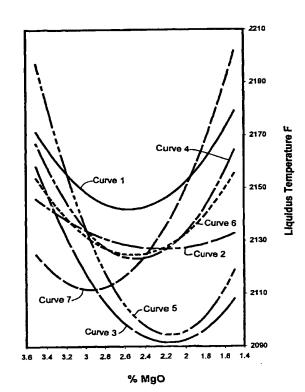
- (74) Agents: SIMINERIO, Andrew, C.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 et al. (US).
- (81) Designated States (national): CA, JP, US.
- (84) Designated States (regional): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:

- With international search report.
- Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: GLASS FIBER COMPOSITION



(57) Abstract: The present invention provides a glass fiber composition comprising: 52 to 62 percent by weight SiO₂, 0 to 2 percent by weight Na₂O, 16 to 25 percent by weight CaO, 8 to 16 percent by weight Al₂O₃, 0.05 to 0.80 percent by weight Fe₂O₃, 0 to 2 percent by weight K₂O, 1.7 to 2.6 percent by weight MgO, 0 to 10 percent by weight B2O3, 0 to 2 percent by weight TiO₂, 0 to 2 percent by weight BaO, 0 to 2 percent by weight ZrO2, and 0 to 2 percent by weight SrO, and further including at least one material selected from the group consisting of: 0.05 to 1.5 percent by weight Li₂O, 0.05 to 1.5 percent by weight ZnO, 0.05 to 3 percent by wight MnO, and 0.05 to 3 percent by weigt MnO₂, wherein the glass composition has a forming temperature of no greater than 2280 °F based on an NIST714 reference standard and a liquidus temperature of no greater than 2155 °F. In one nonlimiting embodiment of the invention, the SiO₂ content is 57 to 59 percent by weight, the Na₂O content is up to 1 percent by weight, the CaO content is 22 to 24 percent by weight, the Al₂O₃ content is 12 to 14 percent by weight, the Fe₂O₃ content is up to 0.4 percent by weight, and the K₂O content is up to 0.1 percent by weight, and the composition includes at least one material selected from the group consisting of: 0.2 to 1 percent by weight Li₂O, 0.2 to 1 percent by weight ZnO, up to 1 percent by weight MnO, and up to 1 percent by weight MnO2.

WO 00/73231 AJ

GLASS FIBER COMPOSITION

Cross Reference to Related Patent Application

This application claims the benefit of U.S. Provisional Application No. 60/136,538, filed May 28, 1999.

Background of the Invention

1. Field of the Invention

The present invention relates to glass compositions for making glass fibers, and more particularly to glass compositions having lowered liquidus and forming temperatures.

2. <u>Technical Considerations</u>

The most common glass composition for making continuous glass fiber 15 strands for textiles and glass fiber reinforcements is "E" glass. The requirements as to what type of composition constitutes an E-glass composition are included in ASTM D578-98. An advantage of using E-glass is that its liquidus temperature is well below its forming temperature, i.e. typically greater than 100°F (56°C) and generally between 150°F (83°C) to 200°F (111°C). As used herein, the terms "forming temperature" and "T_{FORM}" 20 mean the temperature of the glass at which the viscosity of the glass is log 3, or 1000 poise, and the terms "liquidus temperature" and "Tuo" mean the temperature at which solid phase (crystals) and liquid phase (melt) are in equilibrium. The difference between T_{FORM} and T_{LIO}, referred to herein as "delta T" or "\(\Delta \text{T"}\), is a common measure of the crystallization potential of a 25 given melt composition. In the glass fiber forming industry, ΔT is typically maintained at a temperature of at least 90°F (50°C) in order to prevent devitrification of the molten glass in the bushing area of a glass fiber forming operation.

Boron and fluorine containing glass were developed to meet these operating conditions. More specifically, the boron and fluorine were included

10

20

25

in the glass batch materials to act as fluxes during the glass melting operation. However, these materials are volatilized during melting and boron and fluorine emissions are released to the atmosphere. Since boron and fluorine are considered pollutants, these emissions are closely controlled by 5 environmental regulations, which, in turn, requires careful control of the furnace operations and the use of expensive pollution control equipment. In response to this, low boron and/or low fluorine E-glasses were developed. As used herein, "low boron" means that the glass composition is no greater than 5 weight percent boron, and preferably boron-free and "low fluorine" means that the glass composition is no greater than 1 weight percent fluorine, and preferably is fluorine-free.

For example, U.S. Patent No. 3,929,497 discloses a boron-free and fluorine-free glass composition containing titanium dioxide in the range of 0.5 to 5 percent by weight and Fe₂O₃ in the range of 5 to 15 percent by weight.

- 15 U.S. Patent No. 4,199,364 discloses a boron-free and fluorine-free glass composition that contains Li₂O in the range of 0.1 to 1.5 percent by weight and may also include barium oxide. The liquidus temperature of the compositions is over 2200°F.
 - U.S. Patent No. 4,542,106 discloses a boron-free and fluorine-free glass composition that contains 1 to 5 percent by weight TiO2. The fibers also have a seed count of 5 seeds or less per cubic centimeter of glass and an electrical leakage value of 2.8 nanoamperes or less.
 - U.S. Patent No. 5,789,329 discloses a boron-free and fluorine-free glass composition that contains up to 0.9 percent by weight TiO2 and has a ΔT of at least 100°F (56°C).

For additional information concerning glass compositions and methods for fiberizing the glass composition, see K. Loewenstein, The Manufacturing Technology of Continuous Glass Fibres, (3d Ed. 1993) at pages 30-44, 47-60, 115-122 and 126-135, and F. T. Wallenberger (editor), Advanced Inorganic

5

10

15

20

25

<u>Fibers: Processes, Structures, Properties, Applications,</u> (2000) at pages 81-102 and 129-168, which are hereby incorporated by reference.

Because the actual fiber forming operation is conducted at high temperatures, there are high energy costs associated with its production. In addition, the high temperatures accelerate the degradation of the refractory used in the glass melting furnace as well as the bushings used to form the fibers. The bushings include precious metals that cannot be recovered from the glass as the bushings corrode. It would be advantageous to produce the glass fibers at the lowest possible forming and liquidus temperatures so as to reduce the energy costs and thermal load on the furnace refractory and bushings, while at the same time provide the ΔT required to ensure an uninterrupted glass fiber forming operation. Reducing the forming and liquidus temperatures of the glass compositions can also result in environmental benefits, such as but not limited to, a reduction in the amount of fuel required to generate the energy necessary for the fiber forming operation, as well as a reduction in the flue gas temperature. In addition, it would be advantageous if the glass compositions are low fluoride and/or low boron compositions, and preferably are fluorine-free and/or boron-free, so as to reduce or eliminate the environmental pollutants associated with these materials.

Summary of the Invention

The present innovation provides a glass fiber composition comprising: 52 to 62 percent by weight SiO₂, 0 to 2 percent by weight Na₂O, 16 to 25 percent by weight CaO, 8 to 16 percent by weight Al₂O₃, 0.05 to 0.80 percent by weight Fe₂O₃, 0 to 2 percent by weight K₂O, 1.7 to 2.9 percent by weight MgO, 0 to 10 percent by weight B₂O₃, 0 to 2 percent by weight TiO₂, 0 to 2 percent by weight BaO, 0 to 2 percent by weight ZrO₂, and 0 to 2 percent by weight SrO, wherein the glass composition has a forming temperature of no

- 4 -

greater than 2280°F based on an NIST 714 reference standard and a liquidus temperature of no greater than 2155°F. In one nonlimiting embodiment of the invention, the glass fiber composition . further includes at least one material selected from the group consisting of: 0.05 to 1.5 percent by weight Li₂O, 0.05 to 1.5 percent by weight ZnO, 0.05 to 3 percent by weight MnO, and 0.05 to 3 percent by weight MnO₂.

5

15

20

The present invention also provides a glass fiber composition consisting essentially of: 52 to 62 percent by weight SiO₂, 0 to 2 percent by weight Na₂O, 16 to 25 percent by weight CaO, 8 to 16 percent by weight Al₂O₃, 0.05 to 0.80 percent by weight Fe₂O₃, 0 to 2 percent by weight K₂O, 2.2 to 2.9 percent by weight MgO, 0 to 10 percent by weight B₂O₃, 0 to 2 percent by weight TiO₂, 0 to 2 percent by weight BaO, 0 to 2 percent by weight ZrO₂, and 0 to 2 percent by weight SrO, wherein the glass composition has a forming temperature of no greater than 2280°F based on an NIST 714 reference standard and a liquidus temperature of no greater than 2155°F.

The present innovation provides a glass fiber composition comprising: 52 to 62 percent by weight SiO₂, 0 to 2 percent by weight Na₂O, 16 to 25 percent by weight CaO, 8 to 16 percent by weight Al₂O₃, 0.05 to 0.80 percent by weight Fe₂O₃, 0 to 2 percent by weight K₂O, 1.7 to 2.6 percent by weight MgO, 0 to 10 percent by weight B₂O₃, 0 to 2 percent by weight TiO₂, 0 to 2 percent by weight BaO, 0 to 2 percent by weight ZrO₂, and 0 to 2 percent by weight SrO, and further including at least one material selected from the group consisting of: 0.05 to 1.5 percent by weight Li₂O, 0.05 to 1.5 percent by weight ZnO, 0.05 to 3 percent by weight MnO, and 0.05 to 3 percent by weight MnO₂, wherein the glass composition has a forming temperature of no greater than 2280°F based on an NIST 714 reference standard and a liquidus temperature of no greater than 2155°F. In one nonlimiting embodiment of the invention, the SiO₂ content is 57 to 59 percent by weight, the Na₂O content is up to 1 percent by weight, the CaO content is 22 to 24 percent by weight, the

5

10

Al₂O₃ content is 12 to 14 percent by weight, the Fe₂O₃ content is up to 0.4 percent by weight, and the K₂O content is up to 0.1 percent by weight, and the composition includes at least one material selected from the group consisting of: 0.2 to 1 percent by weight Li₂O, 0.2 to 1 percent by weight ZnO, up to 1 percent by weight MnO, and up to 1 percent by weight MnO₂.

Brief Description of the Figure

Figures 1 and 2 are graphs showing the relation between the amount of MgO and the liquidus temperature for glass fiber compositions of the present invention.

Detailed Description of the Invention

The base composition for the glass fibers of the present invention suitable for textiles and glass fiber reinforcements includes the following main constituents in weight percent (wt%) based on the total weight of the final glass composition.

	broad range	preferred range	most preferred range
SiO ₂ (wt%)	52 to 62	55 to 61	57 to 59
Na₂O (wt%)	0 to 2	up to 1.5	up to 1
CaO (wt%)	16 to 25	20 to 25	22 to 24
Al_2O_3 (wt%)	8 to 16	11 to 14	12 to 14
Fe_2O_3 (wt%)	0.05 to 0.80	up to 0.5	up to 0.4
K₂O (wt%)	0 to 2	up to 1	up to 0.1

It should be appreciated that numerical values discussed herein, such as but not limited to weight percent of materials, length of time or temperatures, are approximate and are subject to variations due to various factors well known to those skilled in the art such as, but not limited to, measurement standards, equipment and techniques. For example, where it states in the present application that the range for SiO₂ is 52 to 62 weight percent, this range is about 52 to about 62 weight percent, and where it

states that the forming temperature of a glass composition should be no greater than 2280°F (1249°C), the temperature is about 2280°F.

MgO is also a main constituent of the glass compositions of the present invention. It has been found that the heating and melting profile of a glass fiber composition, and in particular the liquidus temperature, can be controlled and in particular optimized by controlling the amount of MgO, which an object of the present invention and will be discussed later in more detail.

Oftentimes additional materials are added to the glass composition to modify the melt properties of the glass. For example, and without limiting the present invention, Li₂O, ZnO₂, MnO and MnO₂ can be added to the glass fiber composition to reduce T_{LiQ}. In one nonlimiting embodiment of the glass fibers of the present invention, the glass composition can include one or more of these materials in the following amounts.

	broad range	preferred range
Li₂O (wt%)	0.05 to 1.5	0.2 to 1
ZnO (wt%)	0.05 to 1.5	0.2 to 1
MnO (wt%)	0.05 to 3	up to 1
MnO_2 (wt%)	0.05 to 3	up to 1

15

20

25

10

It is believed that levels of these materials less than 0.05 wt% would be considered either tramp amounts or so low that they will not materially impact the glass melt properties.

Boron is another material that can be added to glass fiber compositions to reduce T_{LIQ} . However, as discussed earlier, the inclusion of boron results in the production of particulates that, depending on the particulate level, may have to be removed from a melting furnace exhaust stream before being released into the environment. Although the amount of B_2O_3 in a glass fiber composition can be as high as 10 wt%, one nonlimiting embodiment of a glass composition of the present invention includes no greater than 3 wt% B_2O_3 , preferably no greater than 2 wt% B_2O_3 , and more

preferably no greater than 1 wt% B_2O_3 . In another nonlimiting embodiment of the invention, the glass composition is essentially boron-free, i.e. it includes no more than a trace amount of B_2O_3 , which is considered herein to be up to 0.05 wt% B_2O_3 , and preferably does not include any B_2O_3 .

It should be appreciated that glass fiber compositions can include other constituents and the present invention contemplates the inclusion of other materials in the glass fiber compositions, such as but not limited to, 0 to 2 wt% each of TiO₂, BaO, ZrO₂ and SrO.

5

10

15

20

25

In addition, because of the environmental concerns discussed earlier, although not limiting in the present invention, the glass compositions are preferably low fluorine compositions, i.e. no greater than 0.30 wt% fluorine, and more preferably are fluorine-free, i.e. it includes no more than a trace amount of fluorine, which is considered herein to be up to 0.05 wt% fluorine, and preferably does not include any fluorine.

It should be appreciated that the glass compositions disclosed herein can also include small amounts of other materials, for example melting and refining aids, tramp materials or impurities. For example and without limiting the present invention, melting and fining aids, such as SO₃, are useful during production of the glass, but their residual amounts in the glass can vary and have no material effect on the properties of the glass product. In addition, small amounts of the additives discussed above can enter the glass composition as tramp materials or impurities included in the raw materials of the main constituents.

Commercial glass fibers of the present invention can be prepared in the conventional manner well known in the art, by blending the raw materials used to supply the specific oxides that form the composition of the fibers. For example, typically sand is used for SiO₂, clay for Al₂O₃, lime or limestone for CaO, and dolomite for MgO and some of the CaO. As discussed earlier, the glass can include other additives that are added to modify the glass

properties as well as small amounts of melting and refining aids, tramp materials or impurities.

5

10

15

20

25

After the ingredients are mixed in the proper proportions to provide the desired weight of each constituent for the desired glass, the batch is melted in a conventional glass fiber melting furnace and the resulting molten glass is passed along a conventional forehearth and into a glass fiber forming bushing located along the bottom of the forehearth, as is well known to those skilled in the art. During the glass melting phase, the glass is typically heated to a temperature of at least 2550°F (1400°C). The molten glass is then drawn or pulled through a plurality of holes in the bottom of the bushing. The streams of molten glass are attenuated to filaments by winding a strand of filaments on a forming tube mounted on a rotatable collet of a winding machine. Alternatively, the fiber forming apparatus can be, for example, a forming device for synthetic textile fibers or strands in which fibers are drawn from nozzles, such as but not limited to a spinneret, as is known to those skilled in the art. Typical forehearths and glass fiber forming arrangements are shown in K. Loewenstein, The Manufacturing Technology of Continuous Glass Fibres, (Third Edition 1993) at pages 85-107 and pages 115-135, which are hereby incorporated by reference.

Tables 1-7 show laboratory examples of glass fiber compositions that illustrate the effect of MgO on the liquidus temperature of the glass compositions. Boron and fluorine were not included in these compositions. The glass fiber compositions shown in Tables 1-7 were prepared from reagent grade oxides (e.g., pure silica or calcia). The batch size for each example was 1000 grams. The individual batch ingredients were weighed out, combined and placed in a tightly sealed jar. The sealed jar was then placed in a paint shaker for 15 minutes to effectively mix the ingredients. A portion of the batch was then place into a platinum crucible, filling no more than 3/4 of its volume. The crucible was then placed in a furnace and heated

- 9 -

to 2600°F (1425°C) for 15 minutes. The remaining batch was then added to the hot crucible and heated to 2600°F (1425°C) for 15 to 30 minutes. The furnace temperature was then raised to 2700°F (1482°C) and held there for 4 hours. The molten glass was then fritted in water and dried. The forming temperature, i.e. the glass temperature at a viscosity of 1000 poise, was determined by ASTM method C965-81, and the liquidus temperature by ASTM method C829-81.

The weight percent of the constituents of the compositions shown in Tables 1-7 are based on the weight percent of each constituent in the batch. It is believed that the batch weight percent is generally about the same as the weight percent of the melted sample, except for glass batch materials that volatilize during melting, e.g. boron and fluorine. For boron, it is believed that the weight percent of B₂O₃ in a laboratory samples will be 5 to 10 percent less than the weight percent of B₂O₃ in the batch composition. For fluorine, it is believed that the weight percent of fluorine in a lab melt will be about 50 percent less than the weight percent of fluorine in the batch composition. It is further believed that glass fiber compositions made from commercial grade materials and melted under conventional operating conditions will have similar batch and melt weight percents as discussed above, except that the batch and melt weight percents for the volatile components of the composition will actually be closer to each other than the batch and melt wt% of the laboratory melts because in a conventional melting operation, the materials are exposed to the high melting temperatures for less time than the 4 hours of exposure for the laboratory melts.

20

25

Determination of the high temperature viscosity, T_{FORM}, was based on the glass samples being compared against physical standards supplied by the National Institute of Standards and Testing (NIST). In Tables 1-7, T_{FORM} is reported based on comparison to either NIST 717A, which is a borosilicate glass standard, or NIST 714, which is a soda lime glass standard. Although

either standard can be used, it is believed that the NIST 714 reference standard is more reliable because it has been observed that the NIST borosilicate standard 717A deteriorates at temperatures greater than 2150°F (1177°C). In comparing T_{FORM} based on the two different standards, generally T_{FORM} based on NIST 714 is 20°F to 25°F (11°C to 16°C) higher than T_{FORM} based on NIST 717A. The T_{LIQ} is unaffected by the NIST standard.

10

20

25

Examples 1-7 in Table 1 show the change in the liquidus temperature of a typical glass fiber forming composition that further includes 1 wt% TiO₂, as the amount of MgO is varied from 1.82 to 3 wt%. Examples 8-14 in Table 2 and Examples 15-30 in Table 3 show the change in the liquidus temperature of a typical glass fiber forming composition that further includes 1.5 or 1.1 wt% TiO₂, respectively, and 0.90 wt% Li₂O, as the amount of MgO is varied from 1.7 to 3.5 wt%. Examples 31-38 in Table 4 show the change in the liquidus temperature of a typical glass fiber forming composition that further includes 0.5 wt% TiO₂ and 0.90 wt% Li₂O, as the amount of MgO is varied from 1.7 to 3.12 wt%. Examples 39-49 in Table 5 show the change in the liquidus temperature of a typical glass fiber forming composition that further includes 1.1 wt% TiO₂, 0.45 wt% Li₂O and 0.45 wt% ZnO, as the amount of MgO is varied from 1.7 to 3.1 wt%. Examples 47-54 in Table 6 show the change in the liquidus temperature of a typical glass fiber forming composition that further includes 1.1 wt% TiO₂ and 0.90 wt% ZnO, as the amount of MgO is varied from 1.7 to 3.1 wt%. Examples 59-66 in Table 7 show the change in the liquidus temperature of a typical glass fiber forming composition that further includes 1.1 wt% TiO₂, 0.30 wt% Na₂O, 0.60 wt% Li₂O and 0.25 wt% Fe₂O₃ as the amount of MgO is varied from 1.7 to 3.1 wt%. In addition, the forming temperatures for selected glass compositions are also included in Tables 1-7.

Tables 1-7 also include the ratio SiO₂/RO, which is the ratio of the silica content of the batch, expressed as SiO₂, to the sum of the calcia and magnesia content, expressed as CaO and MgO, respectively.

TABLE 1

	Ex. 1	Ex. 2*	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7
SiO ₂ (wt%)	59.83	59.61	60.13	60.43	60.43	59.61	59.61
Al ₂ O ₃ (wt%)	12.21	12.16	12.27	12.39	12.33	12.16	12.16
CaO (wt%)	22.80	23.51	22.92	23.14	23.03	24.31	24.31
MgO (wt%)	3.00	2.62	2.50	2.00	2.00	1.82	1.82
TiO ₂ (wt%)	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Na₂O (wt%)	0.96	0.90	0.98	1.01	1.01	0.90	0.90
Fe ₂ O ₃ (wt%)	0.20	0.20	0.20	0.20	0.20	0.20	0.20
SiO₂/RO	2.32	2.28	2.37	2.40	2.41	2.28	2.28
T _{FORM} (°F) @ NIST 714		2265	2309				2278
T _{LIQ} (°F)	2160	2138	2127	2149	2154	2161	2182
ΔT (°F)		127	182				94

^{*} average of five samples

TABLE 2

	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14
SiO _z (wt%)	59.62	59.30	59.97	60.09	60.21	60.33	60.75
Al ₂ O ₃ (wt%)	12.12	12.10	12.19	12.22	12.24	12.24	12.35
CaO (wt%)	22.12	22.60	22.25	22.30	22.34	22.39	22.55
MgO (wt%)	3.50	3.40	2.90	2.70	2.50	2.30	1.70
TiO ₂ (wt%)	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Li₂O (wt%)	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Fe ₂ O ₃ (wt%)	0.25	0.20	0.25	0.25	0.25	0.25	0.25
SiO₂/RO	2.33	2.28	2.38	2.40	2.42	2.44	2.51
NIST 717A							
T _{FORM} (°F)	2196		2197	2192	2196	2223	2239
T _{LIQ} (°F)	2158	2136	2122	2152	2124	2120	2131
ΔT (°F)	38		75	40	72	103	108
NIST 714							
T _{FORM} (°F)	2219		2223	2215	2219	2248	2264
T _{LIQ} (°F)	2158	2136	2122	2152	2124	2120	2131
ΔT (°F)	61		101	63	95	128	133

TABLE 3

	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20	Ex. 21	Ex. 23
SiO ₂ (wt%)	59.61	59.61	59.73	59.85	59.97	60.09	60.10	60.10
Al ₂ O ₃ (wt%)	12.92	12.92	12.92	12.95	12.97	13.00	13.00	13.00
CaO (wt%)	21.91	21.96	22.00	22.04	22.09	22.13	22.15	22.15
MgO (wt%)	3.50	3.30	3.10	2.90	2.70	2.50	2.50	2.50
TiO ₂ (wt%)	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
Li₂O (wt%)	0.90	0.90	0.90	0.90	0.90	0.90	0.9	0.9
Fe ₂ O ₃ (wt%)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
SiO ₂ /RO	2.35	2.36	2.38	2.40	2.42	2.44	2.44	2.44
NIST 717A			-					
T _{FORM} (°F)								
T _{LIQ} (°F)	2154	2138	2127	2122	2120	2111		
ΔT (°F)					_			
NIST 714				_				
T _{FORM} (°F)	2215	2215	2217	2217	2226	2233	2255	2259
T _{uo} (°F)	2154	2138	2127	2122	2120	2111	2070	2077
ΔT (°F)	61	77	90	95	106	122	185	182

- 13 -

TABLE 3 (cont.)

	Ex. 23	Ex. 24	Ex. 25	Ex. 26	Ex. 27	Ex. 28	Ex. 29	Ex. 30
SiO ₂ (wt%)	60.21	60.00	60.33	59.95	60.00	59.90	60.57	59.85
Al ₂ O ₃ (wt%)	13.02	12.40	13.05	12.40	12.50	12.40	13.10	12.0
CaO (wt%)	22.18	22.05	22.22	23.30	23.70	23.55	22.31	23.80
MgO (wt%)	2.30	2.30	2.10	2.10	1.90	1.90	1.70	1.70
TiO ₂ (wt%)	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
Li₂O (wt%)	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Fe ₂ O ₃ (wt%)	0.25	0.25	0.25	0.25	0.25	0.25	0.26	0.25
SiO ₂ /RO	2.46	2.46	2.48	2.36	2.34	2.35	2.52	2.35
NIST 717A								
T _{FORM} (°F)	2226	2221	2273	2223	2237		2235	2210
T _{LIQ} (°F)	2088	2095	2077	2106	2082	2120	2086	2113
ΔT (°F)	138	126	196	117	155		149	97
NIST 714					·			
T _{FORM} (°F)	2251	2246	2296	2248	2262	2235	2262	2235
T _{LIQ} (°F)	2088	2095	2077	2106	2082	2113	2086	2113
ΔT (°F)	163	151	219	142	180	122	176	122

TABLE 4

	Ex. 31	Ex. 32	Ex. 33	Ex. 34	Ex. 35	Ex. 36	Ex. 37	Ex. 38
SiO ₂ (wt%)	60.05	59.97	60.09	60.21	60.23	60.23	60.33	60.76
Al ₂ O ₃ (wt%)	12.98	12.19	12.22	12.24	12.25	12.25	12.27	12.35
CaO (wt%)	22.14	23.56	23.31	23.35	23.36	23.36	23.40	23.56
MgO (wt%)	3.12	2.90	2.70	2.50	2.50	2.50	2.30	1.70
TiO ₂ (wt%)	0.55	0.50	0.50	0.50	0.51	0.51	0.50	0.50
Li ₂ O (wt%)	0.91	0.90	0.90	0.90	0.9	0.9	0.90	0.90
Fe ₂ O ₃ (wt%)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
SiO₂/RO	2.38	2.27	2.31	2.33	2.33	2.33	2.35	2.41
NIST 717A								
T _{FORM} (°F)	2264	2181	2197	2192			2196	2201
T _{LIQ} (°F)	2136	2138	2125	2124	2120	2116	2131	2149
ΔT (°F)	128	43	72	68			65	52
NIST 714								
T _{FORM} (°F)		2205	2223	2215	2228	2235	2221	2226
T _{LIQ} (°F)	2136	2138	2125	2124	2120	2116	2131	2149
ΔT (°F)		68	98	91	108	119	90	77

TABLE 5

	Ex. 39	Ex. 40	Ex. 41	Ex. 42	Ex. 43	Ex. 44	Ex. 45	Ex. 46	Ex. 47	Ex. 48	Ex. 49
SiO ₂ (wt%)	59.73	59.85	59.97	60.09	60.21	60.33	59.54	60.45	59.47	60.57	59.40
Al ₂ O ₃ (wt%)	12.92	12.95	12.97	13.00	13.02	13.05	12.16	13.08	12.16	13.10	12.16
CaO (wt%)	22.00	22.04	22.09	22.13	22.18	22.22	23.95	22.27	24.22	22.31	24.49
MgO (wt%)	3.10	2.90	2.70	2.50	2.30	2.10	2.10	1.90	1.90	1.70	1.70
TiO ₂ (wt%)	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
Li₂O (wt%)	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
ZnO (wt%)	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45	0.45
Fe ₂ O ₃ (wt%)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
SiO₂/RO	2.38	2.40	2.42	2.44	2.46	2.48	2.29	2.50	2.28	2.52	2.27
NIST 717A											
T _{FORM} (°F)	2242	2248	2250	2259	2257	2273	2241	2273		2278	2248
T _{LIQ} (°F)	2142	2134	2109	2097	2091	2084	2111	2082	2118	2075	2134
ΔT (°F)	100	114	141	162	166	189	130	191		203	114
NIST 714							-				-
T _{FORM} (°F)	2268	2275	2275	2284	2284	2300	2266	2300	2224	2305	2273
Tuo (°F)	2142	2134	2109	2097	2091	2084	2111	2082	2118	2075	2134
ΔT (°F)	124	141	166	187	193	216	155	218	106	230	139

- 16 -

TABLE 6

	Ex. 50	Ex. 51	Ex. 52	Ex. 53	Ex. 54	Ex. 55	Ex. 56	Ex. 57	Ex. 58
SiO ₂ (wt%)	59.73	59.85	59.97	58.80	60.09	60.21	60.33	60.45	60.57
Al ₂ O ₃ (wt%)	12.92	12.95	12.97	13.33	13.00	13.02	13.05	13.08	13.10
CaO (wt%)	22.00	22.04	22.09	23.45	22.13	22.18	22.22	22.27	22.31
MgO (wt%)	3.10	2.90	2.70	2.50	2.50	2.30	2.10	1.90	1.70
TiO ₂ (wt%)	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
ZnO (wt%)	0.90	0.90	0.90	0.9	0.90	0.90	0.90	0.90	0.90
Fe ₂ O ₃ (wt%)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
SiO ₂ /RO	2.38	2.40	2.42	2.27.	2.44	2.46	2.48	2.50	2.52
NIST 717A								_	
T _{FORM} (°F)	2282	2286	2296	2287	2304	2296	2307	2316	2298
T _{LIQ} (°F)	2138	2131	2118	2129	2115	2131	2136	2128	2140
ΔT (°F)	144	155	178	158	189	165	171	178	158
NIST 714						-			
T _{FORM} (°F)	2309	2313	2323	2314	2332	2323	2336	2345	2327
T _{LIQ} (°F)	2138	2131	2118	2129	2115	2131	2136	2138	2140
ΔT (°F)	171	182	205	185	217	192	200	207	187

WO 00/73231

15

TABLE 7

	Ex. 59	Ex. 60	Ex. 61	Ex. 62	Ex. 63	Ex. 64	Ex. 65	Ex. 66
SiO ₂ (wt%)	59.80	59.75	59.70	59.65	59.60	59.55	59.50	59.45
Al ₂ O ₃ (wt%)	12.25	12.25	12.25	12.25	12.25	12.25	12.25	12.25
CaO (wt%)	22.69	22.85	22.85	23.35	23.60	23.85	24.10	24.35
MgO (wt%)	3.10	2.90	2.70	2.50	2.30	2.10	1.90	1.70
TiO ₂ (wt%)	1.10	1.10	1.10	1.10	1.10	1.10	1.10	1.10
Na₂O (wt%)	0.30	0.30	0.30	0.30	0.30	0.30	0.30	0.30
Li ₂ O (wt%)	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Fe ₂ O ₃ (wt%)	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
SiO₂/RO	2.33	2.32	2.34	2.31	2.30	2.29	2.29	2.28
NIST 717A								
T _{FORM} (°F)	2239		2242	2232	2235	2228	2228	2228
T _{LIQ} (°F)	2113	2113	2111	2118	2133	2143	2158	2178
ΔT (°F)	126		131	113	103	85	70	50
NIST 714		-						
T _{FORM} (°F)	2264	2257	2268	2257	2260	2253	2253	2253
T _{LIQ} (°F)	2113	2113	2111	2118	2133	2143	2158	2178
ΔT (°F)	151	144	157	139	127	110	95	75

Figures 1 and 2 present curves illustrating the relationship between the forming temperature of the compositions shown in Tables 1-7 versus the amount of MgO, as discussed below in more detail. These curves are 2nd order polynomial curves generated using Microsoft® Excel 97 SR-2(f). Each of the curves shows that the amount of MgO impacts the liquidus temperature and in particular, there is a eutectic, i.e. minimum, in the liquidus temperature vs. the amount of MgO, indicating that the amount of MgO can be controlled to generate a minimum liquidus temperature for a glass fiber forming composition.

More specifically, Curve 1 in Figure 1 illustrates the relationship between the liquidus temperature and the amount of MgO in the glass compositions shown in Examples 1-7 in Table 1. In order to expand the MgO range to 3.5 weight percent, a control composition was also included in the curve. The control composition included 59.37 wt% SiO₂, 12.94 wt% Al₂O₃,

21.00 wt% CaO, 3.5 wt% MgO, 1.42 wt% TiO_2 , 1.01 wt% NaO and 0.22 wt% Fe_2O_3 , and had a T_{LiQ} of 2158°F. As can be seen, based on this curve, the liquidus temperature approaches a minimum in the range of 2.2 to 2.9 wt% MgO, and reaches a minimum temperature at 2.45 to 2.65 wt% MgO.

5

Curve 2 in Figure 1 illustrates the relationship between the liquidus temperature and the amount of MgO in the glass compositions shown in Examples 8-14 in Table 2. As can be seen, based on this curve, the liquidus temperature approaches a minimum in the range of 1.85 to 2.6 wt% MgO, and reaches a minimum temperature at 2.0 to 2.45 wt% MgO.

10

Curve 3 in Figure 1 illustrates the relationship between the liquidus temperature and the amount of MgO in the glass compositions shown in Examples 15-30 in Table 3. As can be seen, based on this curve, the liquidus temperature approaches a minimum in the range of 1.8 to 2.5 wt% MgO, and reaches a minimum temperature at 2.0 to 2.3 wt% MgO.

15

Curve 4 in Figure 1 illustrates the relationship between the liquidus temperature and the amount of MgO in the glass compositions shown in Examples 31-38 in Table 4. As can be seen, based on this curve, the liquidus temperature approaches a minimum in the range of 2.3 to 2.7 wt% MgO, and reaches a minimum temperature at 2.35 to 2.6 wt% MgO.

20

Curve 5 in Figure 1 illustrates the relationship between the liquidus temperature and the amount of MgO in the glass compositions shown in Examples 39-49 in Table 5. As can be seen, based on this curve, the liquidus temperature approaches a minimum in the range of 1.8 to 2.5 wt% MgO, and reaches a minimum temperature at 2.0 to 2.3 wt% MgO.

25

Curve 6 in Figure 1 illustrates the relationship between the liquidus temperature and the amount of MgO in the glass compositions shown in Examples 50-58 in Table 6. As can be seen, based on this curve, the liquidus temperature approaches a minimum in the range of 2.3 to 2.7 wt% MgO, and reaches a minimum temperature at 2.4 to 2.6 wt% MgO.

10

20

Curve 7 in Figure 1 illustrates the relationship between the liquidus temperature and the amount of MgO in the glass compositions shown in Examples 59-66 in Table 7. The control sample discussed above was incorporated into Curve 7. As can be seen, based on this curve, the liquidus temperature approaches a minimum in the range of 2.7 to 3.2 wt% MgO, and reaches a minimum temperature at 2.8 to 3.1 wt% MgO.

As can be seen in Curves 1-7, the amount of MgO impacts the liquidus temperature and in particular, the amount of MgO can be controlled to generate a minimum liquidus temperature for a glass fiber forming composition.

Figure 2 Illustrates the relationship between the liquidus temperature and the amount of MgO for various combinations of Examples 8-58 in Tables 2-6. More specifically, Curve A plots the liquidus temperature versus the amount of MgO for the glass compositions shown in Tables 2, 3, and 4, 15 Curve B plots the liquidus temperature versus the amount of MgO for the glass compositions shown in Tables 3, 5 and 6, and Curve C plots the liquidus temperature versus the amount of MgO for the glass compositions shown in Tables 2-6. It is appreciated that Curves A, B and C combine the liquidus temperature for different glass compositions. More specifically, the glass compositions represented by Curve A have the same Li₂O level but differ in the amount of TiO2, the glass compositions represented by Curve B have the same amount of TiO, but differ in the amount of Li₂O and ZnO (although the total amount of Li₂O+ZnO is the same), and the glass compositions represented by Curve C differ in the amounts of TiO2, Li2O and/or ZnO. However, these combinations are offered to illustrate the trend in the liquidus temperature as the amount of MgO varies.

Referring to Figure 2, it can be seen that the liquidus temperature for Curves A, B and C approaches a minimum in the range of 1.7 to 2.65 wt% MgO, and reaches a minimum temperature at 1.90 to 2.55 wt% MgO:

The fact that the glass compositions of Tables 2-6 exhibit a minimum liquidus temperature (as shown in Curves 2-6, A, B and C) than the glass compositions of Table 1 (as shown in Curve 1) is to be expected since Examples 8-58 in Tables 2-6 all included additives, and in particular, Li₂O and/or ZnO, which reduce liquidus temperature. However, of particular significance is the fact that the minimum liquidus temperatures for the glass compositions of Tables 2-6 are generally within an MgO range lower than that of the glass compositions of Table 1.

In viewing Curves 1-7 and A-C in Figures 1 and 2, it is clear that the amount of MgO impacts the heating and melting profile of a glass fiber forming compositions, and in particular, the MgO content can be used to minimize the liquidus temperature of a glass fiber forming composition and allow for a lower forming temperature while maintaining the ΔT required to facilitate a continuous and uninterrupted glass fiber forming operation.

10

15

Examples 67-98 in Table 8 are additional examples of glass compositions of the present invention having 2.3 to 2.55 wt% MgO and a ΔT of greater than 90°F based on a NIST 714 reference standard. These laboratory samples include up to 3 wt% B_2O_3 , up to 0.9 wt% Na_2O , up to 1.1 wt% TiO_2 , up to 0.9 wt% Li_2O , up to 1 wt% ZnO, up to 3 wt% MnO_3 based on their batch composition, as discussed earlier. The samples were made in the same manner as those in Tables 1-7.

- 21 -

TABLE 8

				,				
	Ex. 67	Ex. 68**	Ex. 69	Ex. 70	Ex. 71	Ex. 72	Ex. 73	Ex. 74
SiO ₂ (wt%)	60.12	59.61	59.11	58.61	60.12	59.01	59.31	59.61
Al ₂ O ₃ (wt%)	13.00	12.16	12.16	12.16	13.00	12.04	12.10	12.16
CaO (wt%)	21.13	23.50	23.00	23.50	21.13	23.27	23.38	23.50
MgO (wt%)	2.50	2.50	2.50	2.50	2.50	2.48	2.49	2.50
TiO ₂ (wt%)	1.10	1.10	1.10	1.10	1.10	1.09	1.09	1.10
B ₂ O ₃ (wt%)	1.00	0.30	1.00	1.00	1.00	1.00	0.50	0.50
Na₂O (wt%)						0.89	0.89	
Li₂O (wt%)		0.20	0.90	0.90	0.90			0.50
ZnO (wt%)	0.90	0.20						
MnO (wt%)		0.20						
MnO₂ (wt%)								
Fe ₂ O ₃ (wt%)	0.25	0.23	0.23	0.23	0.25	0.23	0.23	0.23
SiO₂/RO	2.54	2.29	2.32	2.25	2.54	2.29	2.29	2.29
NIST 717A								
T _{FORM} (°F)	2235	2247	2178	2172	2318	2260	2255	2221
T _{LIQ} (°F)	2082	2099	2088	2088	2172	2152	2154	2111
ΔT (°F)	153	148	90	79	146	108	101	110
NIST 714								
T _{FORM} (°F)	2260	2272	2201	2194	2345	2286	2280	2246
T _{LIQ} (°F)	2082	2099	2088	2088	2172	2152	2154	2111
ΔT (°F)	178	173	113	106	173	134	126	135

^{**} average of two samples

- 22 -

TABLE 8 (cont.)

	Ex. 75	Ex. 76	Ex. 77	Ex. 78	Ex. 79**	Ex. 80**	Ex. 81**	Ex. 82
SiO ₂ (wt%)	59.40	59.20	59.61	59.61	59.61	57.72	59.61	58.61
Al ₂ O ₃ (wt%)	12.16	12.16	12.16	12.16	12.16	11.80	12.16	12.16
CaO (wt%)	23.49	23.69	23.50	23.50	20.50	22.80	20.50	23.50
MgO (wt%)	2.30	2.30	2.50	2.50	2.50	2.52	2.50	2.50
TiO ₂ (wt%)	1.10	1.10	1.10	1.10	1.10	1.07	1.10	1.10
B ₂ O ₃ (wt%)		•	0.30	0.45				1.00
Na₂O (wt%)	0.40	0.40			0.90	0.87	0.90	
Li₂O (wt%)	0.45	0.45	0.30					0.30
ZnO (wt%)	0.45	0.45	0.30	0.45				0.30
MnO (wt%)		ľ			3.00			0.30
MnO ₂ (wt%)					Ì	3.00	3.00	
Fe ₂ O ₃ (wt%)	0.25	0.25	0.23	0.23	0.23	0.22	0.23	0.23
SiO₂/RO	2.30	2.28	2.29	2.29	2.59	2.28	2.59	2.25
NIST 717A								
T _{FORM} (°F)	2246	2250	2235	2271	2221	2196	2224	2226
T _{LIQ} (°F)	2118	2105	2113	2113	2117	2125	2118	2082
ΔT (°F)	128	145	122	158	104	71	106	144
NIST 714			-					
T _{FORM} (°F)	2273	2277	2260	2298	2245	2219	2249	2251
T _{LIQ} (°F)	2118	2105	2113	2113	2117	2125	2118	2082
ΔT (°F)	155	172	147	185	128	94	131	169

^{**} average of two samples

- 23 -

TABLE 8 (cont.)

	Ex. 83	Ex. 84	Ex. 85	Ex. 86	Ex. 87	Ex. 88	Ex. 89	Ex. 90
SiO ₂ (wt%)	58.96	58.70	58.35	57.65	58.15	57.95	58.20	58.10
Al ₂ O ₃ (wt%)	13.24	13.35	13.20	13.40	13.20	13.20	13.03	13.03
CaO (wt%)	23.65	23.50	23.65	24.15	22.85	24.05	23.64	23.74
MgO (wt%)	2.5	2.50	2.55	2.55	2.55	2.55	2.50	2.50
TiO₂ (wt%)	.50	0.50	1.10	1.10	1.10	1.10	0.50	0.50
B ₂ O ₃ (wt%)				*				
Na₂O (wt%)		0.30						
Li₂O (wt%)	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
ZnO (wt%)					1.00	1.00	1.00	1.00
MnO (wt%)								
MnO ₂ (wt%)								
Fe ₂ O ₃ (wt%)	0.25	0.25	0.25	0.25	0.25	0.25	0.23	0.23
SiO₂/RO	2.25	2.26	2.23	2.16	2.29	2.18	2.23	2.21
NIST 717A								-
T _{FORM} (°F)								
Tuo (°F)								
ΔT (°F)						,		
NIST 714								
T _{FORM} (°F)	2214	2212	2212	2203	2205	2183	2201	2203
T _{LIQ} (°F)	2116	2107	2095	2109	2077	2084	2098	2091
ΔT (°F)	98	105	117	94	128	99	103	112

10

TABLE 8 (cont.)

	Ex. 91	Ex. 92	Ex. 93	Ex. 94	Ex. 95	Ex. 96	Ex. 97	Ex. 98
SiO ₂ (wt%)	58.00	58.10	58.30	57.60	56.25	55.75	56.00	57.75
Al ₂ O ₃ (wt%)	13.03	13.03	13.03	13.23	13.20	13.20	13.60	13.20
CaO (wt%)	23.84	23.74	23.54	23.84	23.75	23.25	24.25	24.25
MgO (wt%)	2.50	2.50	2.50	2.50	2.50	2.55	2.50	2.55
TiO ₂ (wt%)	0.50	0.50	0.50	0.50	1.10	1.10	0.50	1.10
B ₂ O ₃ (wt%)	1.00	1.00	1.00	1.20	2.00	3.00	2.00	
Na₂O (wt%)				0.10	0.90	0.90	0.90	0.90
Li₂O (wt%)	0.90	0.90	0.90	0.80				
ZnO (wt%)								
MnO (wt%)								
MnO₂ (wt%)					,			
Fe ₂ O ₃ (wt%)	0.23	0.23	0.23	0.23	0.25	0.25	0.25	0.25
SiO₂/RO	2.20	2.21	2.24	2.19	2.14	2.16	2.09	2.15
NIST 717A		·						
T _{FORM} (°F)								-
T _{LiQ} (°F)							"	- "
ΔT (°F)								
NIST 714								
T _{FORM} (°F)	2178	2181	2183	2185	2235	2199	2215	2250
T _{LIQ} (°F)	2079	2075	2084	2071	2100	2060	2077	2131
ΔT (°F)	99	106	99	114	135	139	138	119

Table 9 includes several glass fiber melt compositions made in a commercial glass melting operation. The amount of each constituent in the table is the weight percent in the actual melt. The weight percent for the Li₂O was determined using wet chemical analysis techniques, the weight percent for the B₂O₃ was determined using Neutron Transmission analysis techniques, and the weight percent for the remaining constituents was determined using X-ray fluorescence analysis (also referred to as "XRF analysis"), all of which are well know to those skilled in the art.

WO 00/73231

TABLE 9

	Ex. 99	Ex. 100	Ex. 101	Ex. 102
SiO ₂ (wt%)	57.97	56.83	58.57	58.46
Al ₂ O ₃ (wt%)	12.28	13.28	12.44	12.32
CaO (wt%)	24.15	23.71	23.85	23.70
MgO (wt%)	2.6	2.45	2.42	2.48
TiO ₂ (wt%)	1.16	0.55	0.51	0.50
B ₂ O ₃ (wt%)		2.10	1.37	1.2
Na₂O (wt%)	0.89	0.87		
Li₂O (wt%)			0.84	0.88
K₂O (wt%)	0.06	0.06	0.07	0.07
Fe ₂ O ₃ (wt%)	0.28	0.28	0.27	0.275
SiO₂/RO	2.17	2.17	2.23	2.23
NIST 714				
T _{FORM} (°F)	2253	2224	2183	2185
T _{LIQ} (°F)	2140	2061	2082	2080
ΔT (°F)	113	164	101	105

Based on the above, in one nonlimiting embodiment of the present invention, the glass fiber compositions have a base composition of SiO_2 , CaO, Al_2O_3 and Fe_2O_3 , and optionally Na_2O , as discussed above, and a MgO content ranging from 1.7 to 2.9 wt%, preferably from 1.8 to 2.9 wt%, and more preferably 1.8 to 2.7. In another nonlimiting embodiment, the glass fiber compositions have a MgO content ranging from 1.7 to 2.7 wt%, and preferably from 1.9 to 2.65 wt%.

In one nonlimiting embodiment of the invention, for glass compositions that do not include any liquidus temperature reducing additives other than MgO or only trace amounts of these additive, i.e. less than 0.05 wt, the MgO range is 2.2 to 2.9, preferably from 2.4 to 2.8 wt%, and more 2.45 to 2.65 wt%. In another embodiment of glass compositions with little or no liquidus temperature reducing additives other than MgO, the MgO range is from 2.2 to 2.7, and preferably from 2.3 to 2.6 wt%.

In still another nonlimiting embodiment of the invention, in glass compositions that include a total amount of at least 0.05 wt% of liquidus temperature lowering additives, the MgO content ranges from 1.7 to 2.65 wt%, and preferably between 1.8 and 2.6 wt%, and more preferably 1.9 to 2.55 wt%. In another nonlimiting embodiment of glass compositions that include liquidus temperature lowering additives, the MgO content ranges from 1.7 to 2.5 wt%, and preferably between 1.8 and 2.3 wt%. In one nonlimiting embodiment of the present invention, the liquidus temperature lowering additives in the glass fiber compositions include, but are not limited to, Li₂O, ZnO, MnO, MnO₂ and/or B₂O₃ in the amounts discussed earlier.

10

20

25

It should be appreciated that although other commercially available glasses reduce environmental hazards due to boron and fluorine emissions by reducing or eliminating these materials from the batch, these glasses are processed at higher forming temperatures that conventional E-glass. As a result, they require additional energy for production. The present invention provides glass compositions that include little or no boron and/or fluorine and have a forming temperature generally lower than other low boron and/or fluorine glass compositions, and boron-free and fluorine-free glass compositions, and more specifically, have forming temperatures approaching that of E-glass. In one nonlimiting embodiment of the invention, the forming temperature of the glass compositions of the present invention should be no greater than 2280°F (1249°C), and preferably no greater than 2260°F (1238°C), and more preferably no greater than 2230°F (1221°C), based on the NIST 714 reference standard. In one particular nonlimiting embodiment of the invention, the forming temperature is no greater than 2200°F (1204°C), based on the NIST 714 reference standard.

5

15

20

25

In addition, in one nonlimiting embodiment of the present invention, the liquidus temperature of the glass compositions of the present invention should be no greater than 2155°F (1179°C), and preferably no greater than 2145°F (1174°C), and more preferably no greater than 2130°F (1166°C).

As discussed earlier, in the glass fiber forming industry, ΔT shouldbe maintained in a range sufficient to prevent devitrification of the molten glass in the bushing area of a glass fiber forming operation and stagnant areas of the glass melting furnace. In the present invention, it ΔT should be at least 65°F (36°C), preferably at least 90°F (50°C), and more preferably at least 100°F (56°C). In addition, although not required, in order to maintain the overall heating and melting requirements of the glass fiber composition low, it is preferred that ΔT be no greater than 150°F (83°C) and more preferably no greater than 125°F (69°C). This will maintain a lower forming temperature for a given liquidus temperature and result in good energy efficiency. If required, the amounts of SiO₂ and CaO can be modified to change the forming temperature and provide a desired ΔT. More specifically, reducing the silica content while simultaneously maintaining or increasing the calcia content (thus reducing the SiO₂/RO ratio) will reduce the forming temperature and thus reduce ΔT. This type of modification would be of value if, for example, ΔT was much greater than 100°F and could be reduced without adversely affecting the glass melting and forming operation. Conversely, increasing the silica content and while simultaneously maintaining or reducing the calcia content (thus increasing the SiO₂/RO ratio) will raise the forming temperature and thus increase ΔT . This type of modification would be of value if, for example, ΔT was too low and had to be increased to at least 100°F. Compositional adjustments of the silica and/or calcia (and the resulting SiO₂/RO ratio) in

either direction are possible until the ΔT is obtained that is deemed to facilitate the pursuit of a safe industrial melt forming process.

As discussed above, the $\mathrm{SiO_2/RO}$ ratio can be manipulated to further assist in achieving the goal of lowering the overall processing temperature, and in particular lowering the forming temperature while providing a ΔT required to facilitate continuous fiber forming operation. Although not limiting in the present invention, the glass fiber compositions of the present invention have an $\mathrm{SiO_2/RO}$ ratio of no greater than 2.3, preferably no greater than 2.2.

The invention has been described with reference to specific embodiments, but it should be understood that variations and modifications that are known to those of skill in the art may be resorted to within the scope of the invention as defined by the claims.

- 29 -

I CLAIM:

1. A glass fiber composition comprising:

SiO₂ 52 to 62 percent by weight; Na₂O 0 to 2 percent by weight; CaO 16 to 25 percent by weight; Al_2O_3 8 to 16 percent by weight; Fe₂O₃ 0.05 to 0.80 percent by weight; K₂O 0 to 2 percent by weight; MgO 1.7 to 2.9 percent by weight; B_2O_3 0 to 10 percent by weight; TiO, 0 to 2 percent by weight; BaO 0 to 2 percent by weight; ZrO₂ 0 to 2 percent by weight; and SrO 0 to 2 percent by weight,

- wherein the glass composition has a forming temperature of no greater than 2280°F based on an NIST 714 reference standard and a liquidus temperature of no greater than 2155°F.
- The glass fiber composition according to claim 1, wherein the
 composition further includes at least one material selected from the group consisting of:

Li₂O 0.05 to 1.5 percent by weight
ZnO 0.05 to 1.5 percent by weight
MnO 0.05 to 3 percent by weight
MnO₂ 0.05 to 3 percent by weight

The glass fiber composition according to claim 2, wherein the MgO content is 1.9 to 2.65 percent by weight, the glass composition has a
 B₂O₃ content of no greater than 3 percent by weight, and the glass composition has a ratio of SiO₂ to RO of no greater than 2.3.

10

15

- 4. The glass fiber composition according to claim 1, wherein the MgO content is 1.8 to 2.7 percent by weight.
- 5 5. The glass fiber composition according to claim 4, wherein the MgO content is 1.9 to 2.65 percent by weight.
 - 6. The glass fiber composition according to claim 1, wherein the glass composition has a B_2O_3 content of no greater than 3 percent by weight.

7. The glass fiber composition according to claim 1, wherein the glass composition has a ratio of SiO₂ to RO of no greater than 2.3.

8. A glass fiber composition consisting essentially of:

SiO₂ 52 to 62 percent by weight;

Na₂O 0 to 2 percent by weight;

CaO 16 to 25 percent by weight;

Al₂O₃ 8 to 16 percent by weight;

Fe₂O₃ 0.05 to 0.80 percent by weight;

 K_2O 0 to 2 percent by weight;

MgO 2.2 to 2.9 percent by weight;

 B_2O_3 0 to 10 percent by weight;

TiO₂ 0 to 2 percent by weight;

BaO 0 to 2 percent by weight;

ZrO₂ 0 to 2 percent by weight; and

SrO 0 to 2 percent by weight,

wherein the glass composition has a forming temperature of no greater than 2280°F based on an NIST 714 reference standard and a liquidus temperature of no greater than 2155°F.

- 9. The glass fiber composition according to claim 8, wherein the SiO_2 content is 55 to 61 percent by weight, the Na_2O content is up to 1.5 percent by weight, the CaO content is 20 to 25 percent by weight, the Al_2O_3 content is 11 to 14 percent by weight, the Fe_2O_3 content is up to 0.5 percent by weight, and the K_2O content is up to 1 percent by weight.
- 10. The glass fiber composition according to claim 9, wherein the glass composition has a B_2O_3 content of no greater than 3 percent by weight, a ratio of SiO_2 to RO of no greater than 2.3, and ΔT of at least 65°F.

10

5

- 11. The glass fiber composition according to claim 8, wherein the MgO content is 2.4 to 2.7 percent by weight.
- 12. The glass fiber composition according to claim 11, wherein the15 MgO content is 2.45 to 2.65 percent by weight.
 - 13. The glass fiber composition according to claim 8, wherein the glass composition has a ratio of SiO₂ to RO of no greater than 2.3.
- The glass fiber composition according to claim 8, wherein the glass composition has a B_2O_3 content of no greater than 3 percent by weight.
 - 15. The glass fiber composition according to claim 14, wherein the glass composition is essentially free of boron.

25

16. The glass fiber composition according to claim 8, wherein the glass composition has a forming temperature of no greater 2260°F based on an NIST 714 reference standard.

- 17. The glass fiber composition according to claim 16, wherein the glass composition has a liquidus temperature of no greater than 2245°F.
- 18. The glass fiber composition according to claim 8, wherein the composition has a ΔT of at least 65°F.
 - 19. The glass fiber composition according to claim 8, wherein the composition has a ΔT of no greater than 150°F.
- 10 20. A glass fiber composition comprising:

SiO₂ 52 to 62 percent by weight;

Na₂O 0 to 2 percent by weight;

CaO 16 to 25 percent by weight;

Al₂O₃ 8 to 16 percent by weight;

Fe₂O₃ 0.05 to 0.80 percent by weight;

K₂O 0 to 2 percent by weight;

MgO 1.7 to 2.6 percent by weight;

B₂O₃ 0 to 10 percent by weight;

TiO₂ 0 to 2 percent by weight;

BaO 0 to 2 percent by weight;

ZrO₂ 0 to 2 percent by weight; and

SrO 0 to 2 percent by weight,

and further including at least one material selected from the group consisting of:

Li₂O 0.05 to 1.5 percent by weight;

ZnO 0.05 to 1.5 percent by weight;

MnO 0.05 to 3 percent by weight; and

MnO₂ 0.05 to 3 percent by weight,

wherein the glass composition has a forming temperature of no greater than 2280°F based on an NIST 714 reference standard and a liquidus temperature of no greater than 2155°F.

20

- 21. The glass fiber composition according to claim 20, wherein the MgO content is 1.8 to 2.5 percent by weight.
- 5 22. The glass fiber composition according to claim 21, wherein the MgO content is 1.9 to 2.55 percent by weight.
- 23. The glass fiber composition according to claim 22, wherein the SiO₂ content is 57 to 59 percent by weight, the Na₂O content is up to 1

 10 percent by weight, the CaO content is 22 to 24 percent by weight, the Al₂O₃ content is 12 to 14 percent by weight, the Fe₂O₃ content is up to 0.4 percent by weight, and the K₂O content is up to 0.1 percent by weight.
- 24. The glass fiber composition according to claim 23, wherein the composition includes at least one material selected from the group consisting of:

Li₂O	0.2 to 1 percent by weight
ZnO·	0.2 to 1 percent by weight
MnO	up to 1 percent by weight
MnO ₂	up to 1 percent by weight

- 25. The glass fiber composition according to claim 20, wherein the glass composition has a B_2O_3 content of no greater than 2 percent by weight.
- 26. The glass fiber composition according to claim 20, wherein the SiO_2 content is 55 to 61 percent by weight, the Na_2O content is up to 1.5 percent by weight, the CaO content is 20 to 25 percent by weight, the Al_2O_3 content is 11 to 14 percent by weight, the Fe_2O_3 content is up to 0.5 percent by weight, and the K_2O content is up to 1 percent by weight.

- 27. The glass fiber composition according to claim 26, wherein the SiO₂ content is 57 to 59 percent by weight, the Na₂O content is up to 1 percent by weight, the CaO content is 22 to 24 percent by weight, the Al₂O₃ content is 12 to 14 percent by weight, the Fe₂O₃ content is up to 0.4 percent by weight, and the K₂O content is up to 0.1 percent by weight.
- 28. The glass fiber composition according to claim 20, wherein the composition further includes at least one material selected from the group consisting of:

Li₂O	0.2 to 1 percent by weight
ZnO	0.2 to 1 percent by weight
MnO	up to 1 percent by weight
MnO ₂	up to 1 percent by weight

- 29. The glass fiber composition according to claim 20, wherein the glass composition has a B₂O₃ content of no greater than 3 percent by weight.
- 30. The glass fiber composition according to claim 29, wherein the glass composition has a B₂O₃ content of no greater than 2 percent by weight.
 - 31. The glass fiber composition according to claim 30, wherein the glass composition has a B_2O_3 content of no greater than 1 percent by weight.
- 20 32. The glass fiber composition according to claim 31, wherein the glass composition is essentially free of boron.
 - 33. The glass fiber composition according to claim 20, wherein the glass composition has a ratio of SiO₂ to RO of no greater than 2.3.

- 34. The glass fiber composition according to claim 33, wherein the glass composition has a ratio of SiO₂ to RO of no greater than 2.25.
- 35. The glass fiber composition according to claim 34, wherein the glass composition has a ratio of SiO₂ to RO of no greater than 2.2.
 - 36. The glass fiber composition according to claim 20, wherein the glass composition has a forming temperature of no greater than 2260°F based on an NIST 714 reference standard.

- 37. The glass fiber composition according to claim 36, wherein the glass composition has a forming temperature of no greater than 2230°F based on an NIST 714 reference standard.
- 15 38. The glass fiber composition according to claim 37, wherein the glass composition has a forming temperature of no greater than 2200°F based on an NIST 714 reference standard.
- 39. The glass fiber composition according to claim 20, wherein the glass composition has a liquidus temperature of no greater than 2245°F.
 - 40. The glass fiber composition according to claim 39, wherein the glass composition has a liquidus temperature of no greater than 2230°F.
- 25 41. The glass fiber composition according to claim 20, wherein the composition has a ΔT of at least 65°F.
 - 42. The glass fiber composition according to claim 41, wherein the composition has a ΔT of at least 90°F.

WO 00/73231

PCT/US00/14155

- 36 -

43. The glass fiber composition according to claim 41, wherein the composition has a ΔT of no greater than 150°F.

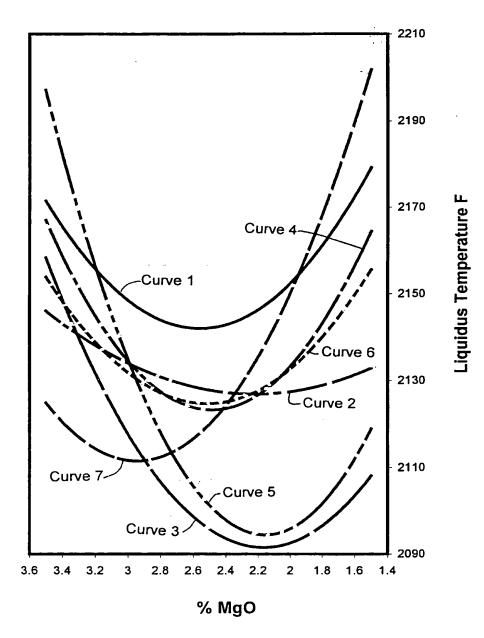


FIGURE 1

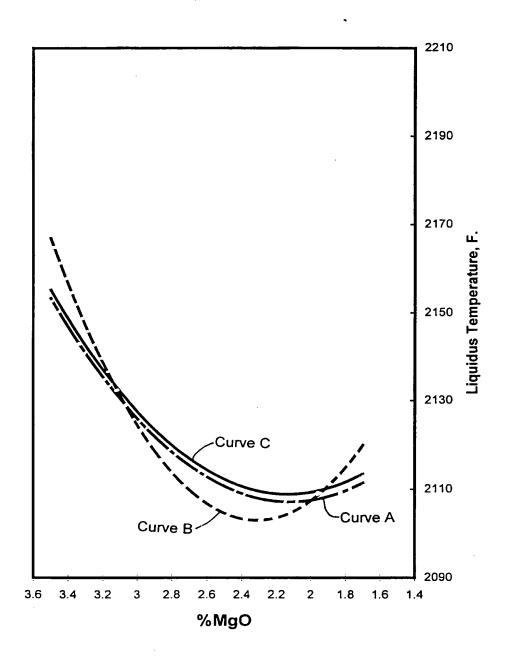


FIGURE 2

INTERNATIONAL SEARCH REPORT

Inte. ional Application No PCT/US 00/14155

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 C03C13/00 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) CO3C IPC 7 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. X DATABASE WPI 1,4-14,Section Ch, Week 199534 16-19 Derwent Publications Ltd., London, GB; Class F01, AN 1995-262260 XP002147163 & RU 2 027 687 C (FOKIN A I), 27 January 1995 (1995-01-27) abstract FR 2 692 248 A (VETROTEX FRANCE SA) 1,4-14, X 17 December 1993 (1993-12-17) 16-19 claims; example 7 X WO 96 39362 A (OWENS CORNING FIBERGLASS 1,4-19 CORP ; EASTES WALTER L (US); HOFMANN DOUGL) 12 December 1996 (1996-12-12) claims: examples -/--Further documents are listed in the continuation of box C. X Patent family members are listed in annex. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person sidiled in the art. citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the International search Date of mailing of the international search report 12 September 2000 21/09/2000 Name and mailing address of the ISA Authorized officer Ruropean Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3018 Reedijk, A

INTERNATIONAL SEARCH REPORT

Inte onal Application No PCT/US 00/14155

	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
K	US 4 066 466 A (NEELY JR HOMER E) 3 January 1978 (1978-01-03) claims	1-43
(FR 2 768 144 A (VETROTEX FRANCE SA) 12 March 1999 (1999-03-12) the whole document	1-43
\	US 4 542 106 A (SPROULL JAMES F) 17 September 1985 (1985-09-17) cited in the application claims	1-43
A	DATABASE WPI Section Ch, Week 198843 Derwent Publications Ltd., London, GB; Class A60, AN 1988-304828 XP002147164 & JP 63 225552 A (NITTO BOSEKI CO LTD), 20 September 1988 (1988-09-20) abstract	1,2,20, 24,28

INTERNATIONAL SEARCH REPORT

formation on patent family members

Inter 'onal Application No
PCT/US 00/14155

Patent document cited in search report		Publication		Patent family	Publication date	
		date		member(s)		
RU	2027687	С	27-01-1995	NONE		
FR	2692248	Α	17-12-1993	NONE		
WO	9639362	A	12-12-1996	AU	692712 B	11-06-1998
				AU	6094896 A	24-12-1996
				BR	9608349 A	28-07-1998
				CA	2223603 A	12-12-1996
				DE	69607614 D	11-05-2000
				DE	69607614 T	27-07-2000
				EP	0832046 A	01-04-1998
				US	5789329 A	04-08-1998
US	4066466	Α	03-01-1978	BE	848490 A	18-05-1977
				CA	1078412 A	27-05-1980
				DE	2650280 A	26-01-1978
				FR	2359089 A	17-02-1978
				GB	1552485 A	12-09-1979
				IT	1069864 B	25-03-198
,				JP	53012917 A	06-02-1978
				NL	7612133 A	24-01-1978
FR	2768144	Α	12-03-1999	AU	9166698 A	29-03-1999
				BR	9806170 A	19-10-1999
				CZ	9901664 A	17-11-1999
				EP	0951457 A	27-10-1999
				WO	9912858 A	18-03-1999
				NO	992227 A	05-07-1999
US	4542106	Α	17-09-1985	CA	1226305 A	01-09-1987
		•	- · · ·	DE	3570860 D	13-07-1989
				EP	0165530 A	27-12-198
				JP	1789670 C	29-09-1993
				JP	3007614 B	04-02-1991
				JP	61014152 A	22-01-1986
JP	63225552	Α	20-09-1988	JP	1756068 C	23-04-1993
				JP	4046911 B	31-07-1992

Form PCT/ISA/210 (patent family annex) (July 1992)